

# PATENT SPECIFICATION

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## (54) A PROCESS FOR THE PRODUCTION OF FINELY DIVIDED OXIDES OF METALS AND/OR SILICON

(71) We, DEUTSCHE GOLD-UND SILBER - SCHEIDEANSTALT, vormalis

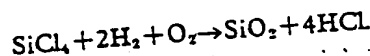
Roessler, a body corporate organised under the laws of Germany, of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of finely divided oxides of metals and/or silicon.

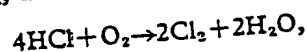
More particularly the invention relates to a process for the production of finely divided oxides of metals, e.g. aluminium, titanium and/or silicon, by hydrolytic reaction of volatile chlorides thereof in a flame, by feeding the chlorides in a mixture with hydrogen, and with air or oxygen to a flame which burns from a burner in a reaction chamber, reacting them in the flame, passing the oxide aerosol formed together with the process gases through a subsequent cooling system and separating the oxide from the process gases in a separation apparatus.

Very finely divided oxides can be produced according to known processes by the hydrolytic combustion of volatile metal halide compounds, by feeding the volatile compounds together with water vapour forming gases and with air or oxygen, either separately or already mixed, to a burner. In these processes air or oxygen and hydrogen are mixed in such a quantitative ratio, that both complete combustion of the hydrogen and hydrolysis of the halide compound are assured. To produce particularly active products the flame temperature is controlled by the addition of an over-stoichiometric amount of air or oxygen or of inert gases, e.g. nitrogen.

The products obtained according to these known processes are produced together with waste gas containing hydrogen halides, which is separated from the oxide particles in a separator. The hydrolysis of the halide takes place using, for example,  $\text{SiCl}_4$ , in accordance with the equation:



Free halogen is generated in a secondary reaction by the partial oxidation of HCl with excess  $\text{O}_2$ , in accordance with the equation:



so that the reaction gas contains 6 to 10% by weight of free chlorine, relative to the HCl content, depending on the way in which the flame reaction is conducted.

The chlorine necessarily occurring as a by-product must be removed by additional technical efforts after the absorption of the hydrogen chloride from the fuel gas. This takes place according to known processes.

Because of the expense of these processes, attempts have been made to influence the formation of chlorine during the pyrolytic reaction. It is known from German Patent Specification No. 1,210,421, that formation of free chlorine can be avoided by conducting the pyrolysis not in the presence of secondary air, but of an inert gas, e.g. nitrogen, since in this case the process works with a so-called self-sufficient flame, i.e. the flame already contains all the necessary components for the reaction in a homogeneously mixed form. It is further known from German Patent No. 1,244,125 expanding on the above mentioned process, that a part of the reaction waste gas can be led off after the separation of solid particles and introduced in measured quantities into an enclosed combustion chamber instead of the so-called secondary air.

Although the formation of free chlorine can to a large extent be prevented according to this known process, the reaction can only be carried out by burning the flame within an inert gas atmosphere or in an enclosed combustion chamber. In another known process (German Offenlegungsschrift 2,153,671) the formation of free halogen is prevented by "enveloping" the flame with an envelope of water vapour, which is produced either by injecting water vapour or by burning off a high  $\text{H}_2$  excess.

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In the latter case it is also necessary to mix nitrogen, to achieve product qualities corresponding to the normal, open method of working. This means that by manipulating the flame (in the reaction chamber) the course of the reaction is adversely affected and additional measures must be taken, in order to attain normal product quality.

An object of the invention is to provide a process for the production of finely divided oxides of metals, e.g. aluminium, titanium and/or silicon, by hydrolytic reaction of volatile chlorides thereof in a flame, by feeding the chlorides in a mixture with hydrogen and with air or oxygen, to a flame burning from a burner in a reaction chamber and reacting them in the flame, passing the oxide aerosol formed, together with the process gases, through a subsequent cooling system and separating the oxide from the process gases in a separation apparatus, in which the difficulties arising from absorbing the much diluted, elementary chlorine from the reaction gases are avoided without interfering with the course of the reaction.

The present invention provides a process for the production of finely divided oxides of metals and/or silicon by the hydrolytic reaction of a volatile chloride thereof in a flame, which comprises feeding the chlorides in a mixture with hydrogen and with air or oxygen to a flame burning from a burner in a reaction chamber, reacting them in the flame, keeping the burner mouth free by passing hydrogen thereover, passing the oxide aerosol thus formed together with process gases through a subsequent cooling system and separating the oxide from the process gases in a separation apparatus, chlorine formed in the flame reaction being reduced with hydrogen during cooling of the reaction gases to a temperature below the reaction temperature of the hydrogen with the oxygen in the reaction gas.

The distinctive feature of the invention is that the chlorine formed in the flame reaction, is reduced with hydrogen during cooling below the reaction temperature of hydrogen with the oxygen contained in the reaction gas.

Reduction of the chlorine with hydrogen can be achieved by the introduction of hydrogen at one or more points into the reaction gas at a temperature of about 500°C, this temperature level being passed through during the cooling of the reaction products. Thorough mixing is promoted during the introduction of the hydrogen by known means, e.g. by the

incorporation of a fitted moulding.

According to another variant of the process, before or after the separation of the solid reaction products the chlorine, but not the oxygen simultaneously present in the reaction gas, is reacted with hydrogen using high energy light (UV light) or a catalyst.

The hydrogen chloride formed in this reaction is absorbed together with the hydrogen chloride formed in the flame hydrolysis according to known processes, and obtained as concentrated hydrochloric acid. In addition to the advantage of this new process, by which the flame reaction can take place undisturbed, its greater economy should also be stressed. As described in the example, neither additional nitrogen nor water vapour and moreover only small quantities of additional hydrogen are required (to keep the burner mouth free). Furthermore the capacity of the installation in normal working remains the same, since the apparatus does not have to be provided with additional gas ballast, as is necessary with the known processes.

The invention is illustrated by the following Example:

#### EXAMPLE.

2,000 Kg  $\text{SiCl}_4$ , 648  $\text{Nm}^3/\text{h}$  hydrogen and 1,900  $\text{Nm}^3/\text{h}$  air were fed to an Aerosol burner, together with 22  $\text{Nm}^3/\text{h}$  hydrogen over the mantel to keep the burner mouth free ("normal" operation), and 705 kg/h of finely divided silica with a specific surface area of 200  $\text{m}^2/\text{g}$  were obtained. 7.5% of the hydrogen chloride to be expected was found as free chlorine in the reaction gases.

70  $\text{Nm}^3/\text{h}$  hydrogen were introduced into the reaction gas which had been cooled to 510°C. This reduced the quantity of free chlorine to 0.07%, relative to the proportion of hydrogen chloride.

The table gives settings for normal operation for the known process according to German Offenlegungsschrift 2,153,671 and for the embodiment according to the invention. It can be seen that with the process of the invention it is possible to work with very low consumption of input materials.

The production of fine particle oxides of aluminium or titanium or mixed oxides thereof with silicon dioxide can take place in a similar manner, mixed oxides being prepared by the simultaneous reaction of the chlorides of the aluminium or titanium optionally together with silicon tetrachloride.

Hydrogen requirement for chlorine-free processes (values 100 % H<sub>2</sub>)

	Nm <sup>3</sup> /h				Total hydrogen	Nitrogen
	Hydrogen in combustion gas mixture	H <sub>2</sub> envelope for keeping the burner mouth clear	Additional hydrogen			
Process for the production of fine particle silicon dioxide						
Normal process (DT-PS 974 793 US-PS 2,990,249 US-PS 3,086,851 US-PS 3,006,738)	648	22	—		670	—
Chlorine-free process (DT-OS 2,153,671)	849	54	—		903	718
Chlorine-free process (according to the invention)	648	22	70		740	—

## WHAT WE CLAIM IS:—

1. A process for the production of finely divided oxides of metals and/or silicon by the hydrolytic reaction of a volatile chloride thereof in a flame, which comprises feeding the chlorides in a mixture with hydrogen and with air or oxygen to a flame burning from a burner in a reaction chamber, reacting them in the flame, keeping the burner mouth free by passing hydrogen thereover, passing the oxide aerosol thus formed together with process gases through a subsequent cooling system and separating the oxide from the process gases in a separation apparatus, chlorine formed in the flame reaction being reduced with hydrogen during cooling of the reaction gases to a tem-

perature below the reaction temperature of the hydrogen with the oxygen in the reaction gas.

2. A process as claimed in Claim 1, wherein the reduction of the chlorine is carried out by the introduction of hydrogen at one or more points into the reaction gas having a temperature of about 500°C.

3. A process as claimed in Claim 1 or 2, wherein the introduction of hydrogen takes place with the optimum mixing of the reaction gases.

4. A process as claimed in Claim 3, wherein mixing of the reaction gases in the cooling system is promoted by means of fitted mouldings.

5. A process as claimed in Claim 1, wherein

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the chlorine is reacted with hydrogen before or after separation of the solid reaction products, using high energy light (UV-light) or a catalyst.

- 5 6. A process as claimed in Claim 1 for the production of a finely divided oxide in which chlorine present in the reaction gases is reduced with hydrogen substantially as described with particular reference to the Example.

7. A finely divided oxide when produced by a process as claimed in any of Claims 1 to 6. 10

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